

TITLE OF THE INVENTION

Method of Preparing Group III-V Compound Semiconductor
Crystal

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a method of
preparing a group III-V compound semiconductor crystal.

10 ~~Particularly, the present invention relates to a method of
preparing a group III-V compound semiconductor crystal in
which carbon is doped.~~

Description of the Background Art

Conventionally, there are various prior arts as set
15 forth in the following regarding the method of preparing a
group III-V compound semiconductor crystal in which carbon
is doped.

20 In Japanese Patent Laying-Open No. 64-79087 (referred
to as "prior art 1" hereinafter), a method of preparing a
carbon-doped GaAs single crystal according to the gradient
freeze method or horizontal Bridgman method (HB method) is
disclosed.

Fig. 6 is a diagram for describing a method of
preparing a carbon-doped GaAs single crystal according to
prior art 1.

Referring to Fig. 6, a graphite boat 51 as a carbon
25 source is arranged at one side in a quartz ampoule 55. Raw

material which is gallium (Ga) 52 is provided in graphite boat 51. Arsenic (As) 57 is provided at the other side in quartz ampoule 55. Quartz ampoule 55 is sealed in vacuum and then installed in an electric furnace to be heated.

5 After the GaAs raw material is synthesized, the temperature is reduced maintaining a constant temperature gradient, whereby a GaAs single crystal is grown.

1 The carbon of graphite boat 51 reacts with oxygen supplied from As_2O_3 , Ga_2O and the like remaining in quartz
10 ampoule 55 to result in gas of CO , CO_2 and the like to be doped into the growing GaAs crystal.

It is described that the doping amount of carbon can be controlled according to the total amount of oxygen in the sealed quartz ampoule 55, the synthesization reaction
15 condition, or single crystal growth condition, and the like.

✓ In Journal of the Japanese Association of Crystal Growth, 1991, Vol. 18, No. 4, pp. 88-95 (referred to as "prior art 2" hereinafter), a method of preparing a
20 carbon-doped GaAs single crystal by the vertical gradient freeze method (VGF method) is disclosed.

Fig. 7 is a diagram for describing a method of preparing a carbon-doped GaAs single crystal according to prior art 2.

25 Referring to Fig. 7, raw material 62 having carbon

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doped in advance, directly synthesized by the LEC method and boron oxide (B_2O_3) 64 are provided in a crucible 61 and sealed in vacuum in a quartz ampoule 65. This is installed in a vertical furnace and heated to melt the raw material and boron oxide. By reducing the temperature in the furnace while maintaining a constant temperature gradient, a GaAs single crystal is grown.

Here, boron oxide containing water of 200ppm spreads around only the periphery of the upper surface of GaAs melt 62. The center area of the upper surface of GaAs melt 62 is exposed to the ambient. According to the method of prior art 2, the upper surface of the melt must be exposed to the ambient to control the stoichiometry of the GaAs melt. The vapor pressure in quartz ampoule 65 is controlled by arsenic 67.

According to this method, the carbon concentration of the crystal depends on the carbon concentration of the raw material.

In U.S. Patent No. 4,999,082 (referred to as "prior art 3" hereinafter), a method of preparing carbon-doped GaAs single crystal by the vertical Bridgman method (VB method) is disclosed.

Fig. 8 is a diagram for describing a method of preparing carbon-doped GaAs single crystal according to prior art 3.

Referring to Fig. 8, a crucible 71 is filled with GaAs raw material 72. After carbon source 73 is arranged outside of crucible 71, a quartz ampoule 75 is sealed. Quartz ampoule 75 is placed in a vertical furnace and heated to melt the raw material. The furnace is moved upwards while substantially maintaining the set temperature profile. By solidifying the raw material from a seed crystal 77, a GaAs single crystal is grown.

According to this method, carbon source 73 is in fluid communication with compound raw material 72 to allow gas transfer.

Japanese Patent Laying-Open No. 3-252399 (referred to as "prior art 4" hereinafter) discloses a method of preparing a semi-insulating GaAs substrate.

Prior art 4 is characterized in that the impurity which becomes the acceptor is doped so as to result in $1 \sim 3 \times 10^{15}$ atoms/cm³ after subtracting the concentration of the impurity which becomes the donor in a GaAs crystal.

Japanese Patent Laying-Open No. 2-74597 (referred to as "prior art 5" hereinafter) discloses a chromium-doped semi-insulating GaAs single crystal and a method of preparing thereof. This prior art 5 is characterized in that carbon is contained having a concentration n_c that satisfies both the relations of:

$$1 \times 10^{15} \text{cm}^{-3} \leq n_c < n_{si} \text{ and } n_{si} - n_c \leq 4.4 \times 10^{15} \text{cm}^{-3}$$

for the residual Si concentration of n_{Si} remaining in the single crystal, with the resistivity of at least $10^6 \Omega \cdot \text{cm}$.

The above-described prior art have various disadvantages. In prior art 1, boron oxide is not used.
5 Therefore, impurity contamination can be expected. Furthermore, since the amount of the carbon source cannot be controlled in this method, it is difficult to control the carbon concentration.

In prior art 2, carbon cannot be doped during the
10 crystal growth since carbon source is not used. There is a problem that the carbon concentration cannot be adjusted during crystal preparation. Furthermore, a part of the carbon in the GaAs melt reacts with oxygen, that is generated as a result of the water in the boron oxide
15 decomposing, to be lost as CO gas. There was a problem that the carbon concentration in the GaAs crystal is lowered.

In prior art 3, it is difficult to control the carbon concentration since the carbon source is located outside
20 the crucible. Furthermore, impurity contamination can be expected since boron oxide is not used.

In prior art 4, carbon is recited as the impurity serving as the acceptor. However, only the doping of zinc and copper is disclosed as the example. There is no
25 description of carbon doping.

Prior art 5 describes a chromium-doped semi-insulating GaAs single crystal containing carbon. However, this prior art 5 is silent about the method of doping carbon.

5 SUMMARY OF THE INVENTION

In view of the foregoing, an object of the present invention is to provide a method of preparing in high reproducibility a group III-V compound semiconductor crystal of favorable electrical characteristics having impurities removed, and in which the amount of doped carbon can easily be adjusted during crystal growth.

According to an aspect of the present invention, a method of preparing a group III-V compound semiconductor crystal is provided. This method of preparing a group III-V compound semiconductor crystal having carbon doped includes the steps of: filling a crucible or boat with compound raw material, solid carbon, and boron oxide; sealing the crucible or boat filled with compound raw material, solid carbon, and boron oxide in an airtight vessel formed of a gas impermeable material; heating and melting the compound material in a sealed state in the airtight vessel; and solidifying the melted compound material to grow a carbon-doped compound semiconductor crystal.

25 Since the crucible or boat is filled with compound

raw material, solid carbon, and boron oxide according to the present invention, the boron oxide softened by heating is brought into contact with at least a portion of the solid carbon in the state where the compound raw material is melted.

According to the present invention, the carbon concentration in the raw material does not have to be adjusted since carbon can be doped during crystal growth. Good controllability of the carbon concentration is obtained. In other words, the target carbon concentration can be obtained in high reproducibility. By using boron oxide which has an impurity removal effect, the contamination of impurities in the crystal can be suppressed to obtain a crystal of favorable electrical characteristics.

Quartz or pBN (pyrolytic boron nitride) and the like can be enumerated as the gas impermeable material.

Preferably, boron oxide contains water.

This is because the water in boron oxide is essential to remove impurities. Furthermore, it is considered that the water in the boron oxide effects the incorporation of carbon into the crystal.

Boron oxide preferably contains water of 10-500 wt ppm.

In the present invention, the amount of solid carbon

to be filled is preferably larger than the amount of carbon doped into the compound semiconductor crystal.

This is to promote reaction using an excessive amount of carbon since the reaction rate of solid carbon is extremely low. Furthermore, consumption of the part of the solid carbon at the gas generation of the carbon compound must be supplied. Thus, by using solid carbon of an amount larger than the total amount of carbon doped into the crystal, the advantage of the present invention works effectively.

Specifically, the amount of solid carbon must be at least ten times, preferably at least 100 times larger than the weight of the carbon doped into the crystal.

In the present invention, it is preferred that the solid carbon is subjected to a heat treatment under reduced pressure before being filled in the crucible or boat.

By this process, the impurity element remaining in carbon is removed to result in a crystal of higher purity.

The pressure in applying a heat treatment on carbon is preferably from 1 Torr to 1×10^{-8} Torr. The appropriate temperature of the heat treatment is 500°C-2000°C. The above-described effect can be obtained by carrying out the heat treatment for at least one hour. It was found that a greater effect can be obtained as the time for the heat

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treatment becomes longer. However, there is very little change in the effect when the time for the heat treatment exceeds 12 hours. Considering that the cost for production is increased as the time for the heat treatment becomes longer, the time period for the heat treatment of not more than 12 hours is appropriate.

In the present invention, it is preferable to keep the compound raw material in its melted state for a certain time period before it is solidified for crystal growth.

By this process, the impurities of Si and the like in the GaAs polycrystalline raw material can be removed by gettering with boron oxide. Although Si of approximately $1 \times 10^{16} \text{cm}^{-3}$ is included as impurities in the raw material synthesized by the HB method, the amount of Si in the GaAs subjected to the above-described process is less than $1 \times 10^{15} \text{cm}^{-3}$, which is below the detection limit of an analyzer. Si of an amount over $1 \times 10^{15} \text{cm}^{-3}$ was detected from those not subjected to the above-described process.

Thus, carbon can be sufficiently melted in the GaAs melt from the solid carbon by the above-described process. This process also provides the advantage that the temperature of the GaAs melt is stabilized, and the carbon concentration and impurity concentration in the melt can be made uniform.

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The above-described effect can be obtained when the holding time period in the melted state of raw material is at least 3 hours. Further favorable characteristics can be obtained stably when the holding time is at least 6 hours.

5 Although a greater effect can be obtained as the holding time becomes longer, the degree of change in the effect gradually becomes smaller when the holding time period exceeds 36 hours. There is very little change in the effect when the holding time exceeds 72 hours. Considering
10 that the cost for production becomes higher as the holding time is increased, the holding time is preferably not more than 72 hours, further preferably not more than 36 hours.

In the present invention, powder carbon can be used as the solid carbon.

15 Powder carbon is advantageous in promoting the reaction due to its greater specific surface area. Increase in the reaction speed allows carbon to be doped efficiently in the crystal.

Also, the amount of carbon to be doped into the
20 crystal can easily be adjusted according to the grain size, the weight, and the like of the used powder. For example, powder of a smaller grain size has a greater specific surface area to increase the reaction speed, whereby the amount of doped carbon is increased.

25 Therefore, the grain size of the powder carbon is

preferably smaller. More specifically, the average grain size is preferably not more than 100 μ m, more preferably not more than 50 μ m. When powder carbon is used, the powder carbon spreads in the boron oxide softened by heating in the state where the compound raw material is melted.

In the present invention, fiber carbon, as well as powder carbon, can be used as the solid carbon.

Fiber carbon is advantageous in that the diameter of the fiber is small and a greater surface area can be obtained to result in a faster reaction speed. It is therefore possible to dope carbon into the crystal efficiently. Also, the amount of carbon doped into the crystal can easily be adjusted according to the diameter or weight of the fiber that is used. Uniform distribution of the carbon concentration can be obtained from the shoulder to the tail of the prepared crystal when fiber carbon is used.

The diameter of the fiber carbon is preferably smaller. Specifically, the average diameter is preferably not more than 50 μ m, more preferably not more than 10 μ m.

Usage of fiber carbon allows carbon to spread in boron oxide that is softened by heating in the state where the compound raw material is melted. Also, the carbon can float above boron oxide to be exposed to the ambient.

In the present invention, bulk carbon can be used as

solid carbon, in addition to powder carbon and fiber carbon.

5 Bulk carbon is advantageous in that the amount of carbon to be doped in the crystal can easily be adjusted by the weight and configuration of the carbon used. Uniform distribution of carbon concentration can be obtained from the shoulder to the tail of the prepared crystal when bulk carbon is used.

10 Bulk carbon is preferably used in a disk shape that is smaller than the inner diameter of the crucible. The amount of doped carbon can easily be controlled by the diameter of the disk.

15 The bulk solid carbon is preferably a sintered compact of carbon powder. The reaction speed is particularly high for the sintered compact of powder having high porosity. Sintered carbon powder is advantageous in distributing carbon uniformly in the crystal.

20 When bulk solid carbon is used, a state can be obtained in which at least a portion of the bulk solid carbon is immersed in the softened boron oxide.

In the present invention, the crucible or boat is preferably formed of pBN (pyrolytic boron nitride).

25 Depending upon the constituent element of the crucible or boat, there is a possibility that boron oxide

or carbon reacts with the crucible to induce contamination of the raw material melt. pBN is most appropriate as the material of the crucible or boat to suppress reaction with boron oxide or carbon.

5 The present invention is particularly effective as a method of doping carbon into a GaAs crystal.

10 The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a diagram for describing an example of a method of preparing a group III-V compound semiconductor crystal according to the present invention.

 Fig. 2 is a diagram showing the state of carrying out crystal growth using a vertical furnace.

20 Fig. 3 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor crystal according to the present invention.

 Fig. 4 is a diagram for describing a further example of a method of preparing a group III-V compound semiconductor crystal according to the present invention.

25 Fig. 5 is a diagram for describing each portion of a crystal.

Fig. 6 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to an example of prior art.

5 Fig. 7 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to another example of prior art.

10 Fig. 8 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to a further example of prior art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

15 Fig. 1 is a diagram for describing an example of preparing a group III-V compound semiconductor crystal according to the present invention.

Referring to Fig. 1, GaAs polycrystalline raw material 2, carbon powder 13 subjected to heat treatment under reduced pressure in advance, boron oxide (B_2O_3) 4, and a seed crystal 7 were placed in a pBN crucible 1. The seed crystal was placed at the bottom portion of the crucible 1. In crucible 1, arrangement was provided so that carbon powder 13 and boron oxide 4 were brought into
25 contact with each other, and also boron oxide 4 and raw

material 2 were brought into contact with each other when the raw material was melted.

Crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Ampoule 5 was sealed under reduced pressure with a quartz cap 6.

Respective conditions of Example 1 are shown in the following Table 1.

Table 1

GaAs polycrystal (raw material)	3kg used
Carbon powder	350 mesh (grain size 45 μ m and below), 100mg used Heat treatment at 1000°C for 6 hours at the pressure of 10 ⁻² Torr
B ₂ O ₃	Water concentration 50 wt ppm, 50g used
pBN crucible	Inner diameter 80mm, entire length 250mm
Solid arsenic	1g used

10

Referring to Fig. 2, the above-described quartz ampoule 5 was heated at the rate of approximately 200°C/hour by a heater 8 using a vertical furnace 50.

During this process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a

film 4a having a thickness of less than 1mm between pBN crucible 1 and GaAs raw material melt 2. The remainder of boron oxide 4 covered the upper surface of GaAs melt 2. The thickness of the boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 5mm. Carbon powder 13 was dispersed in this boron oxide layer 4b.

The condition mentioned above was kept for approximately 36 hours.

Then, heater 8 was moved upwards at the rate of 4mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal is shown in the following Table 2.

Table 2

Crystal diameter	80mm	
Length of $\phi 80\text{mm}$ portion	100mm	
Carbon concentration	Shoulder	$1.4 \times 10^{15} \text{cm}^{-3}$
	Tail	$0.8 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$2.9 \times 10^7 \Omega \text{cm}$
	Tail	$1.5 \times 10^7 \Omega \text{cm}$
Dislocation density	Shoulder	900cm^{-2}
	Tail	1200cm^{-2}

In the present specification, the "shoulder" and "tail" of a crystal corresponds to the relevant portions

shown in Fig. 5.

The role of solid arsenic (As) sealed under reduced pressure in the quartz ampoule in the present example is set forth in the following.

5 The dissociation pressure at the melting point of GaAs is approximately 1 atm. When GaAs is melted, the airtight vessel is filled with As vapor of approximately 1 atm at the temperature of the melting point. This As vapor is generated as a result of the GaAs melt being decomposed. 10 Therefore, the composition of the GaAs melt is shifted from the original composition of Ga:As=1:1 to Ga rich composition. By sealing solid arsenic in the quartz ampoule in addition to GaAs, the shift from the composition of Ga:As=1:1 caused by decomposition of the 15 GaAs melt can be suppressed.

Example 2

Fig. 3 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor crystal of the present invention.

20 Referring to Fig. 3, GaAs polycrystalline raw material 2, carbon fiber 23 subjected to heat treatment under reduced pressure in advance, boron oxide 4, and a seed crystal 7 were placed in a pBN crucible 1. Seed crystal 7 was placed at the bottom portion of the crucible 25 1. In crucible 1, arrangement was provided so that carbon

fiber 23 and boron oxide 4 were brought into contact with each other and also boron oxide 4 and raw material 2 were brought into contact with each other when the raw material was melted.

5 Crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Quartz ampoule 5 was sealed under reduced pressure with a quartz cap 6.

Respective conditions of Example 2 are shown in the following Table 3.

Table 3

GaAs polycrystal (raw material)	10kg used
Carbon fiber	Average diameter 5-8 μ m, 40mg used, Heat treatment at 800°C for 3 hours at the pressure of 10 ⁻⁷ Torr
B ₂ O ₃	Water concentration 70 wt ppm, 100g used
pBN crucible	Inner diameter 105mm, entire length 400mm
Solid arsenic	1.5g used

Quartz ampoule 5 was heated at the rate of approximately 120°C/hour by a heater 8 using a vertical furnace 50, as shown in Fig. 2.

During the process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a film 4a having a thickness of not more than 1mm between pBN crucible 1 and GaAs melt 2. The remainder of boron oxide 4 covered the upper surface of the GaAs melt. This boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 5mm. The carbon fiber 23 was partially dispersed in boron oxide layer 4b on GaAs melt 2, and partially floated. Furthermore, a portion of carbon fiber 23 was present also at the proximity of the interface between GaAs melt 2 and boron oxide layer 4b.

Then, the condition mentioned above was kept for approximately 12 hours.

Then, heater 8 was moved upwards at the rate of 3mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal are shown in the following Table 4.

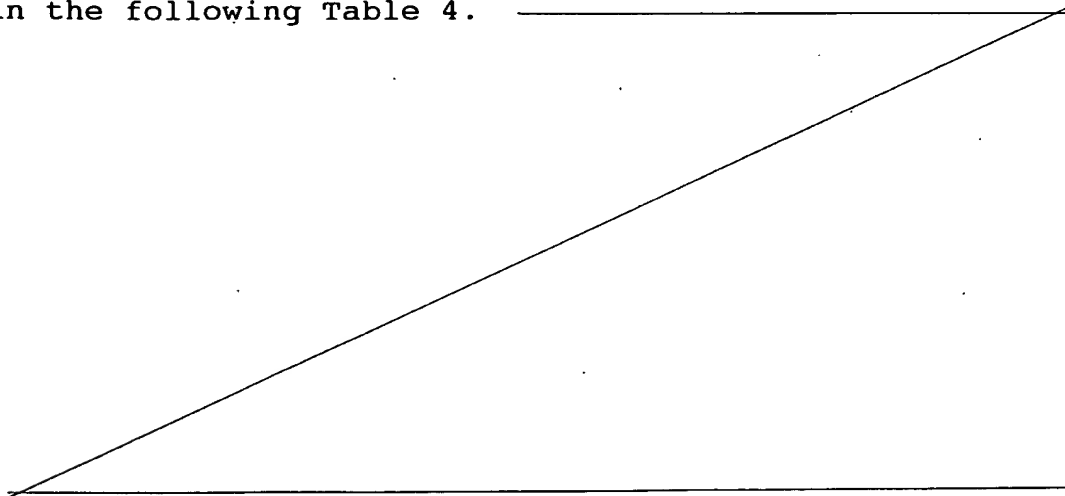


Table 4

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$6.5 \times 10^{15} \text{cm}^{-3}$
	Tail	$7.0 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$4.1 \times 10^8 \Omega \text{cm}$
	Tail	$5.0 \times 10^8 \Omega \text{cm}$
Dislocation density	Shoulder	800cm^{-2}
	Tail	1500cm^{-2}

Example 3

A carbon-doped GaAs single crystal was grown using 20 mg of carbon fiber similar to that of Example 2.

The other conditions of the experiment are identical to those of Example 2, and their description will not be repeated.

The characteristics of the obtained single crystal are shown in the following Table 5.

Table 5

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$2.3 \times 10^{15} \text{cm}^{-3}$
	Tail	$2.2 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$8.8 \times 10^7 \Omega \text{cm}$
	Tail	$8.4 \times 10^7 \Omega \text{cm}$
Dislocation density	Shoulder	1000cm^{-2}
	Tail	1800cm^{-2}

Example 4

A carbon-doped GaAs single crystal was grown using 7.5mg of carbon fiber similar to those of Examples 2 and 3.

The other conditions are identical to those of Examples 2 and 3, and their description will not be repeated.

The characteristics of the obtained single crystal are shown in the following Table 6.

Table 6

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$1.3 \times 10^{15} \text{cm}^{-3}$
	Tail	$1.2 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$2.5 \times 10^7 \Omega \text{cm}$
	Tail	$2.3 \times 10^7 \Omega \text{cm}$
Dislocation density	Shoulder	1500cm^{-2}
	Tail	2000cm^{-2}

It is appreciated from Examples 2, 3 and 4 that the carbon concentration in the crystal can easily be adjusted by just adjusting the amount of solid carbon to be doped according to the present invention.

Example 5

Fig. 4 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor

crystal according to the present invention.

Referring to Fig. 4, GaAs polycrystalline raw material 2, a disk 43 made of sintered carbon powder subjected in advance to a heat treatment under reduced pressure, boron oxide 4, and a seed crystal 7 were placed in a pBN crucible 1. Seed crystal 7 was placed at the bottom portion of the crucible 1. In crucible 1, arrangement was provided so that carbon disk 43 and boron oxide 4 were brought into contact with each other, and also boron oxide 4 and raw material 2 were brought into contact with each other when the raw material was melted.

This crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Quartz ampoule 5 was sealed under reduced pressure using quartz cap 6.

Respective conditions of example 4 are indicated in the following Table 7.

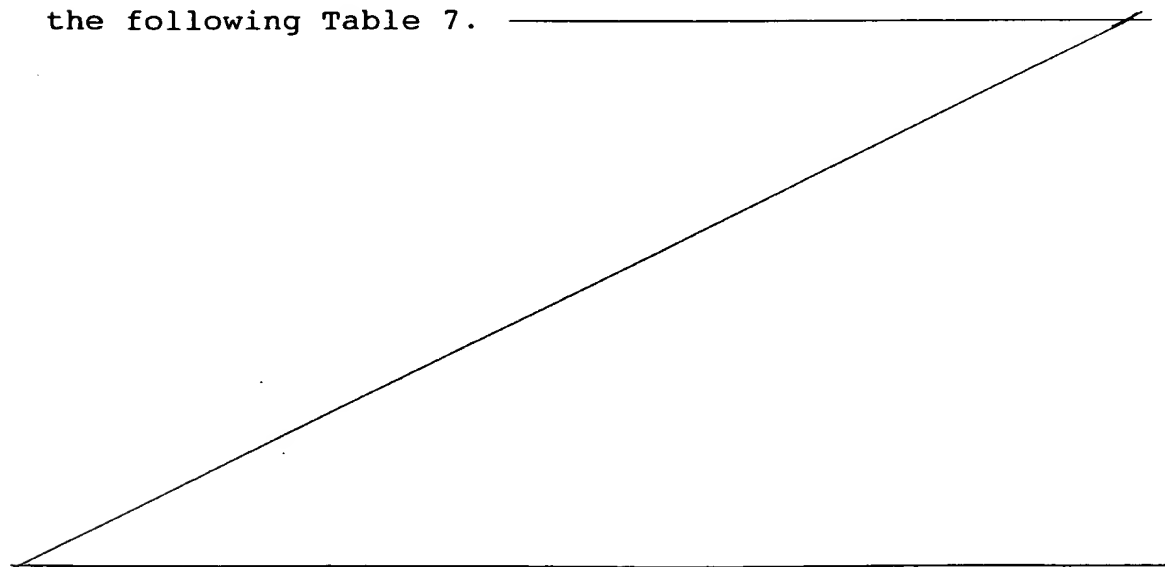


Table 7

GaAs polycrystalline raw material	3kg used
Carbon disk	Diameter 30mm, thickness 10mm used Heat treatment at 1500°C for 12 hours at the pressure of 1 Torr
B ₂ O ₃	Water concentration 300 wt ppm, 50g used
pBN crucible	Inner diameter 80mm, entire length 250mm
Solid arsenic	1g used

The above-described quartz ampoule 5 was heated at the rate of approximately 200°C/hour by heater 8 using vertical furnace 50.

During the process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a film 4a having a thickness of less than 1mm between pBN crucible 1 and GaAs melt 2. The remainder of boron oxide 4 covered the upper surface of GaAs melt 2. The thickness of the boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 6mm. Carbon disk 43 had its bottom surface in contact with raw material melt 2, and its top surface exposed to the ambient. The side surface thereof was surrounded by boron oxide layer 4b.

The condition mentioned above was kept for

approximately 6 hours.

Then, heater 8 was moved upwards at the rate of 4mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal are shown in the following Table 8.

Table 8

Crystal diameter	80mm	
Length of $\phi 80$ mm portion	100mm	
Carbon concentration	Shoulder	$6.8 \times 10^{15} \text{cm}^{-3}$
	Tail	$7.1 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$4.5 \times 10^8 \Omega \text{cm}$
	Tail	$5.2 \times 10^8 \Omega \text{cm}$
Dislocation density	Shoulder	1200cm^{-2}
	Tail	1500cm^{-2}

In a semi-insulating GaAs crystal, the resistivity is one of the most important characteristics. It is preferable that variation in resistivity is smaller. Furthermore, since this resistivity value depends on the carbon concentration in the GaAs crystal, variation in the carbon concentration in the crystal should be as small as possible.

In the above-described examples where carbon fiber or bulk carbon was used as the solid carbon, the carbon was

doped substantially uniformly from the shoulder to the tail of the crystal. It is appreciated that carbon fiber and bulk carbon are preferable as solid carbon sources. The shape of bulk carbon is not limited to the disk shape shown in Example 5, and any shape can be used. Also, bulk carbon is preferably a sintered compact of carbon powder.

Comparison of the effect of the present invention depending upon difference in the type of solid carbon is shown in the following Table 9.

Table 9

Difference in effect among powder, fiber, and bulk carbon

Type of solid carbon	Carbon distribution in a crystal from shoulder to tail
Carbon powder	Gradual decrease of carbon from shoulder to tail
Carbon fiber	Uniform distribution of carbon from shoulder to tail
Bulk carbon	Uniform distribution of carbon from shoulder to tail

Comparison of the carbon concentration in a GaAs crystal between the present invention and the prior art is shown in the following Table 10.

Table 10

Comparison of carbon concentration in GaAs crystal

			Carbon concentration (cm^{-3})	
			Shoulder	Tail
Present invention	Carbon powder		1.4×10^{15}	0.8×10^{15}
	Carbon fiber	Example 2	6.5×10^{15}	7.0×10^{15}
		Example 3	2.3×10^{15}	2.2×10^{15}
		Example 4	1.3×10^{15}	1.2×10^{15}
	Carbon disk		6.8×10^{15}	7.1×10^{15}
Prior art	Prior art 2		0.5×10^{15}	0.4×10^{15}
	Prior art 3		2.2×10^{15}	1.4×10^{15}

5 Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.